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1957

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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THE CORRECT FORM OF THE EQUATION OF CAPILLARY CONDENSATION IN POROUS BODIES AS APPLIED TO DETERMINING THEIR STRUCTURE FROM ADSORPTION AND SORPTION ISOTHERMS, AND CONVERSELY

In the absence of adsorption, the calculation of the vapor-sorption isotherm for a porous body of known structure, as well as the solution of the inverse problem, are possible on the basis of Kelvin' s formula. The presence of adsorption layers complicates the calculation, requiring that their total mass and the difference between half the pore width at the positions of the menisci and the radius of their curvature be taken into account. To overcome the second difficulty, it is customary, when applying Kelvin' s equation, to take this difference as equal to the thickness of the corresponding adsorption layers.

However, I have shown (^{1}) that this method of allowing for the influence of adsorption on capillary condensation is erroneous*, since the curvature of the meniscus surface does not remain constant (dashed line in Fig. 1) up to the surface of the adsorption layers AA, after which it would have to decrease discontinuously; rather, this change in curvature occurs gradually (solid curve) under the influence of the same forces that determine polymolecular adsorption. Let us set forth the derivation of the equation of capillary condensation in porous bodies, exactly applicable when the influence of the curvature of the pore walls on the adsorption equilibrium may be neglected**.

Consider the equilibrium of a sorbent with vapor of pressure p, and denote by: S —the total area of the adsorption layer AA; V—the volume filled by the capillary-condensed phase (in the diagram of Fig. 1, shaded***) with molar volume v; W—the sorption in moles; Γ—the adsorption in mol/cm^2. Let us consider (Fig. 2) a virtual process of "desorption" (at p = const, Γ = const) of $-dW$ moles (shading) by isothermal reversible distillation into a liquid phase with vapor pressure p_0. In this process S increases by dS, while V changes by

$$dV = v(dW - \Gamma\, dS), \tag{1}$$

Fig. 1

Figure 1: Fig. 1

where v is the molar volume of the capillary-condensed phase.

From the definition of the chemical potential, it follows for the corresponding increase in free energy dU:

$$dU = -(\mu_0 - \mu)\, dW, \tag{2}$$

where μ is the chemical potential of the vapor at pressure p; μ_0, at pressure p_0. If U_0 is the free energy of the system at $p = p_0$, when all pores are filled, then

$$U - U_0 = S(\omega - \omega_0) + (s - s_0)\sigma + F - F_0, \tag{3}$$

* A similar error was made by Langmuir in an attempt to take into account the influence of the thickness of wetting films on capillary rise (3).

** The same approach is applicable in the absence of the latter restriction, but leads to considerably less simple formulas (1).

*** The considerations set forth are of a very general nature and are not connected with any special pore shape; in the diagram, for simplicity, a single slit-shaped pore is depicted.

where ω_0 and ω are the free energies per unit area of the interface between the sorbent and the liquid phase and, respectively, of the sorbent (together with the adsorbed film of thickness h) and vapor of pressure p; σ is the surface tension of the liquid at its boundary with the vapor; s is the total area of the menisci in the state under consideration; s_0 is the same at $p = p_0$; F is the excess volume (without taking into account the contribution of the term with ω_0) of the free energy of the capillary-condensed liquid, as compared with the bulk phase; F_0 is the analogous quantity at $p = p_0$. Differentiating (3) at $\omega = \text{const}$, and taking (2) into account, we obtain

$$(\mu_0 - \mu)\, dW = -(\omega - \omega_0)\, dS - \sigma\, ds - dF. \tag{4}$$

Fig. 1

For complete wetting, for a layer of sufficiently large thickness h, $\omega = \omega_0 + \sigma$.

For smaller(1) h,

$$\omega = \omega_0 + \sigma \cos\theta + f(h), \tag{5}$$

where θ is the contact angle;

Fig. 2

Figure 2: Fig. 2

$$f(h) = \int_{h}^{h_0} P(h)\,dh;$$

$P(h)$ is the disjoining pressure$^{(2)}$ of the layer; h_0 is the thickness of the film in equilibrium with saturated vapor$^{(7)}$ ($h_0 \neq \infty$ when $\theta \neq 0$).

Fig. 2

In the simplest case, when it is permissible to neglect the influence of the curvature of the surface of the adsorption layers on their vapor elasticity, i.e., on adsorption equilibrium, we have, introducing the specific volume v:

$$vP(h) = \mu_0 - \mu; \qquad f(h) = \int_{\Gamma}^{\Gamma_0} (\mu_0 - \mu)\,d\Gamma, \tag{6}$$

whence, taking (5) into account, we obtain:

$$\omega - \omega_0 = \sigma\cos\theta + \int_{\Gamma}^{\Gamma_0} (\mu_0 - \mu)\,d\Gamma = \sigma\cos\theta + RT\int_{\Gamma}^{\Gamma_0} \ln\left(\frac{p_0}{p}\right) d\Gamma. \tag{7}$$

It is obvious that the second term on the right-hand side of equation (4) may be neglected when $ds/dS \ll 1$, i.e., when the pore cross sections change smoothly.

The third term on the right-hand side of equation (4) may be omitted under the following conditions: 1) the difference between the densities of the capillary-condensed and the free liquid may be neglected; 2) the width of the slit is so large that the regions of influence of opposite sections of the wall surface on the layer of capillary-condensed liquid enclosed between them do not overlap; 3) the molecular structure does not differ from that of the bulk phase, except for the boundary layers of the first kind, satisfying condition 2.

In this case, from (1), (4), and (7) one may obtain the relation

$$-\frac{dV}{dS} = v\Gamma + \frac{v}{\mu_0 - \mu}\left[\sigma\cos\theta + \int_{\Gamma}^{\Gamma_0} (\mu_0 - \mu)\,d\Gamma\right], \tag{8}$$

or, integrating by parts and transforming:

$$-\frac{dV}{dS} = \frac{v}{\mu_0 - \mu}\left[\sigma\cos\theta + \int_{\mu}^{\mu_0}\Gamma\,d\mu\right] = \frac{v}{RT\ln\frac{p_s}{p}}\left[\sigma\cos\theta + RT\int_{p}^{p_s}\frac{\Gamma}{p}\,dp\right]. \tag{9}$$

The derivative, $-dV/dS$, which has the dimension of length, for the simplest case of a plane slit with nearly parallel walls (for example, near the point of contact of two spheres, or of a sphere and a plane) is equal to $D/2$ (Fig. 1), where D is the width of the slit. In the case of pores of nearly cylindrical shape, $-dV/dS$ is equal to one half of the hydraulic radius. In the general case, $-dV/dS \equiv H$ may be regarded as a measure of the pore width in those sections where the capillary menisci are located. Equation (9) generalizes the Kelvin formula by taking into account the influence of adsorption layers on capillary condensation.

Let us apply this equation to the solution of the following problems:

1. To find the sorption isotherm of vapors by a porous body with a specified structural characteristic, for example, when the function $V = V(H)$ is known,* if the adsorption isotherm of the same vapors on a plane surface of the same nature as the pore walls is known.
2. To find the structural characteristic of a porous body, knowing the vapor sorption isotherm and the isotherm of their adsorption on a plane surface of the same nature as the pore walls.
3. To find, from the sorption isotherm for a porous body of known structure, the pore width at the places where menisci are located as a function of vapor pressure.
4. To find the adsorption isotherm $\Gamma = \Gamma(p)$ from sorption observations in the presence of capillary condensation in a porous body of known structure.

Problem 1. Having determined from (9) $H = -dV/dS$, we can, using the structural characteristic, find V–the volume of filled pores–and, adding $S\Gamma(p)$, find the vapor sorption W for the given vapor pressure p. In this way the sorption isotherm can be constructed point by point.

Problem 2. The change in free energy in an actual (not virtual) equilibrium desorption process can be found directly from the definition of the chemical potential:

$$U - U_s = \int_{W}^{W_0}(\mu_0 - \mu)\,dW, \tag{10}$$

where μ is a function of the variable of integration W.

Comparing (10) with equation (3), in which the second and third terms on the right-hand side are neglected as small, we obtain:

$$S = \frac{\displaystyle\int_{W}^{W_0} (\mu_0 - \mu)\, dW}{\sigma \cos\theta + \displaystyle\int_{\Gamma}^{\Gamma_0} (\mu_0 - \mu)\, d\Gamma} \simeq \frac{RT \displaystyle\int_{W}^{W_0} \left(\ln \frac{p_0}{p}\right) dW}{\sigma \cos\theta + RT \displaystyle\int_{\Gamma}^{\Gamma_0} \left(\ln \frac{p_0}{p}\right) d\Gamma}. \qquad (11)$$

In particular, for the total surface of the sorbent we obtain

$$S_0 \simeq \frac{RT \displaystyle\int_{W_c}^{W_0} \left(\ln \frac{p_0}{p}\right) dW}{\sigma \cos\theta + RT \displaystyle\int_{\Gamma_c}^{\Gamma_0} \left(\ln \frac{p_0}{p}\right) d\Gamma}, \qquad (12)$$

where W_c and Γ_c correspond to any vapor pressure at which capillary condensation is already absent. Of course, if desorption proceeds not entirely at equilibrium (as, for example, in the presence of bottle-shaped pores), then the true S and S_0 are smaller than those calculated from formulas (11) and (12).

We see from (9) and (11) that, knowing $W = W(p)$ and $\Gamma = \Gamma(p)$ from experimental data, it is possible, by simple graphical integration, assigning arbitrary values $p < p_s$, to obtain a series of pairs of corresponding values of S and $H = -dV/dS$. This will make it possible to construct point by point the graph of de–

* For example, from measurements by the mercury-intrusion method.

dependence $-dV/dS$ on S; hence, by graphical integration, one can find $V = V(S)$, and consequently construct the graph of the dependence $V = \Phi(-dV/dS)$.

Problem 3. From equations (8) and (11) we have

$$-Sd\left(\frac{dV}{dS}\right) = \frac{v\, d\mu''}{(\mu_0 - \mu')^2} \int_{W''}^{W_0} (\mu_0 - \mu')\, dW', \qquad (13)$$

where W' is a function of μ'; W'' is a function of μ''.

Taking the integral of both sides of the equation and integrating by parts on the left, while on the right changing the order of integration, we obtain

$$Z \equiv (V_0 - V) - SH = v \int_{W}^{W_0} \frac{(\mu' - \mu)}{(\mu_0 - \mu)}\, dW' = \qquad (14)$$

$$= v(\mu_0 - \mu)^{-1} \int_{W}^{W_0} (\mu' - \mu)\, dW'.$$

Finally, integrating by parts, we obtain:

$$Z = v(\mu_0 - \mu)^{-1} \int_{\mu}^{\mu_0} (W_0 - W')\, d\mu'. \tag{15}$$

If the structure of the body is known, and consequently V and S are known as functions of H, then Z may be regarded as a known function of H: $Z = \Psi(H)$. Then from equation (16) one can find H by the formula:

$$H = \Psi^{-1}\left[\frac{v}{\mu_0 - \mu}\int_{\mu}^{\mu_0} (W_0 - W')\, d\mu'\right], \tag{16}$$

i.e., by graphical integration followed by use of the graph of the dependence of H on Z.

Problem 4. If H is known as a function of p, either by the above-described method for solving problem 3, or from optical observations, as in the experiments of K. V. Chmutov* (5), then the adsorption Γ can be found, as is seen from (9), by the formula:

$$\Gamma = -\frac{1}{v}\frac{d[(\mu_0 - \mu)H]}{d\mu} = -\frac{H}{v} + \frac{(\mu_0 - \mu)}{v}\frac{dH}{d\mu} = -\frac{1}{v}\frac{d(H \ln(p_0/p))}{d\ln(p_0/p)}. \tag{17}$$

In the case where H has been obtained by using the sorption isotherm, it is simpler and more accurate to use the equation

$$\Gamma = \frac{W - V/v}{S},$$

where V and S, by assumption, are known functions of H.

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Received
21 XI 1956

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* Shereshefsky' s experiments, similar in purpose (6), require for their interpretation allowance for the curvature of the walls of the conical capillary used by him.

Note: Figure translations are in progress. See original paper for figures.